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Development of theoretical methods for predicting solvent effects on reactions rates in supercritical water oxidation processes

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6. AUTHOR(S)
Susan C. Tucker

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
University of California, Davis
Davis, CA 95616

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12 a. DISTRIBUTION / AVAILABILITY STATEMENT

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13. ABSTRACT (Maximum 200 words)

The design of efficient supercritical water oxidation reactors for the destruction of chemical warfare agents will be facilitated by computational fluid dynamics modeling of these systems. To assist such modeling efforts, the aim of the present project is to develop computational methods for predicting how reaction rate constants will vary with thermodynamic condition in supercritical water (SCW). Towards this end two reactions were examined in SCW – the anisole hydrolysis reaction and the hydrogen peroxide dissociation reaction. For the anisole reaction the nature of the microscopic viscosity on this reaction was examined as a function of thermodynamic condition and reaction path progress. An interesting interplay of sensitivity to these variables was observed, as were strong local density effects in the compressible regime. However, reaction studies indicate that in spite of the magnitude of the observed compression-induced anomalies, their effect on the reaction rate is expected to be less than a few percent, such that these effects can likely be neglected in reactor modeling. For the hydrogen peroxide dissociation, high-level quantum chemistry calculations suggest that earlier solvation studies on this reaction need to be reconsidered in light of more accurate charge distributions. As well, solvation studies suggest not only that solvation effects may be larger than anticipated for this reaction, especially at very low water densities, but also that polarization may play a critical role, such that standard fixed charge studies will be inaccurate.

14. SUBJECT TERMS

Supercritical water oxidation, supercritical water, supercritical fluids, reaction dynamics, solvation, local density enhancements, multiple time scales, hydrogen peroxide dissociation, anisole hydrolysis, continuum solvation, nonequilibrium solvent effects, viscosity effects, microscopic friction, reactive flux, recrossings

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1. List of Papers

(a) Manuscripts submitted

None this report period. Two additional manuscripts are in progress and should be submitted within the next few months:

"State-point Dependence of the Dynamic Friction on a Molecular Bond in Supercritical Water," A. N. Drozdov, B. Bashore, R. Jendrejack and S. C. Tucker, manuscript in preparation.

"Examination of Nonequilibrium Solvent Effects on an S_N2 Reaction in Supercritical Water," R. Behera, B. Bashore, R. Jendrejack and S. C. Tucker, manuscript in preparation.

(b) Papers published in peer-review journals

D. F. Parsons, B. I. Boone, P. G. Jessop and S. C. Tucker, "Electrostriction Effects on Competing Transition States in Supercritical Fluoroform," , *J. Supercritical Fluids*, (2002) **24**, 173-181.

P. G. Jessop, R. A. Brown, M. Yamakawa, J. Xiao, T. Ikariya, M. Kitamura, S. C. Tucker and R. Noyori, "Pressure-dependent enantioselectivity in the organozinc addition to aldehydes in supercritical fluids," *J. Supercritical Fluids*, (2002) **24**, 161-172.

(c) Papers published in proceedings

None.

(d) Papers presented at meetings (* denotes presenting author)

Invited:

D. F. Parsons and S. C. Tucker*, "Electrostriction Effects on Reactions in Supercritical Water," National Meeting of the American Chemical Society, San Francisco, March 26-30, 2000.

Raghunath Behera, Belinda Bashore, Richard Jendrejak and Susan C. Tucker*, "How local density enhancements influence solute reaction rates in supercritical water," National Meeting of the American Chemical Society, San Diego, CA, April 2001.

Raghunath Behera, Belinda Bashore, Richard Jendrejak and Susan C. Tucker*, "How local density enhancements influence solute reaction rates in supercritical water," EURESCO Molecular Liquids Conference: Water at the New Millenium, Obernai, France, September 2001.

(continued next page)
Raghunath Behera, Belinda Bashore, Richard Jendrejak and Susan C. Tucker*, "How local density enhancements influence solute reaction rates in supercritical water," International Meeting on the Fundamental Aspects of Supercritical Fluids, Kyoto, Japan, December 2001.

Raghunath Behera, Belinda Bashore, Richard Jendrejak and Susan C. Tucker*, "How local density enhancements influence solute reaction rates in supercritical water," National Meeting of the American Chemical Society, Orlando, FL, April 2002.

Contributed:

Raghunath Behera*, Belinda Bashore, Richard Jendrejak and Susan C. Tucker, "How local density enhancements influence solute reaction rates in supercritical water," National Meeting of the American Institute of Chemical Engineers, Reno, NV, Fall 2001.

A. N. Drozdov*, B. Bashore, R. Jendrejack and S. C. Tucker, "State-point Dependence of the Dynamic Friction on a Molecular Bond in Supercritical Water," National Meeting of the American Institute of Chemical Engineers, Reno, NV, Fall 2001.

2. Scientific Personnel Supported

Dr. Drew F. Parsons
Dr. Raghunath Behera
Dr. Nitin Sapre
Dr. Alexander N. Drozdov

3. Report of Inventions

None.

4. Scientific Progress and Accomplishments

Local-Density-Enhancement Effects on Competing Transition States

Combustion, whether in the gas phase or in SCW, involves a series of branched and competing reaction processes. To determine the role played by supercritical solvent compressibility and local density enhancements in supercritical water oxidation (SCWO) during heat-up, cool-down, or other "lower" temperature reactor phases, it is necessary to understand how local density enhancements affect reaction branching from competing transitions states. To examine this question, we considered a model dipolar reaction in supercritical fluoroform, because available experimental results for such a system suggested that local densities could reverse the branching ratios from those expected in the absence of compression. Our work demonstrated that while local density enhancements could, in theory, generate such a reversal in reaction branching ratios, in practice such extreme behavior is highly unlikely to be observed. This result arises because the energetic magnitude of the compression effects is insufficient to overcome the longer-range solvation effects which are not affected by the solvent compression and thus change in more expected ways with density. However, it was found that more moderate compression effects on the branching ratios are likely for dipolar transition states, even down to surprisingly low densities.

Microscopic Viscosity under Supercritical Conditions

We next examined the degree to which reaction-path-dependent local density changes would alter viscosity effects on reactions in SCW under compressible conditions. We again considered a reaction for which experimental rates were available, the hydrolysis of anisole in water under supercritical conditions. At the microscopic level. viscosity effects are controlled by two main parameters of the friction kernel (that is, of the microscopic viscosity action on the reaction coordinate). These are the magnitude and the time scale of the friction. Both of these parameters were found to be sensitive to the temperature, pressure, reaction-path-position and solvent compressibility. In particular, in regions of high solvent compressibility, friction magnitudes increased (at least in the transition state region) and lifetimes lengthened dramatically. Both of these trends suggest that viscosity-induced transition-state recrossings (which would reduce the rate constant from it's expected Transitions State Theory value) might become significant in the compressible regime of SCW.

Viscosity Effects on Reaction Dynamics under Supercritical Conditions

A Reactive-Flux counting techniques was then used to examine the reaction dynamics of the anisole hydrolysis reaction directly, in order to follow up on these suggested effects. The expected solvent-compression-induced viscosity effects were indeed observed. However, the magnitude of the forces due to these effects were found so be insufficient, relative to the magnitude of the underlying potential energy driving force, to cause more than a very limited number of transitions state recrossings. Consequently, the impact of these effects on the reaction rate constants should be small. Consequently, our results suggest that such compression-induced recrossing effects can probably be neglected in SCWO rate calculations without introducing significant error.

Hydrogen Peroxide Dissociation

Subsequent to these more general studies of supercritical solvent effects on reactivity, we began a specific examination of a key player in controlling SCWO rates, the hydrogen peroxide dissociation reaction in SCW. High-level correlated *ab initio* calculations, completed in collaboration with Dr. Peter Taylor at the SDSC, were performed to determine the dependence of the solute charge distribution for this key reaction. It was found that these correlated methods, which reflect the geometric changes of the complex along its reaction path much more accurately than do Density Functional Theory (DFT) calculations, also predict a substantially different reaction-path-dependence for the charge distribution than do the DFT calculations. Additionally, *ab initio* studies of the reactant H_2O_2 complexed with 1 or 2 water molecules, as well as studies of this complex immersed in a dielectric continuum both indicate that polarization effects may alter the solute charges by as much as 30%, suggesting that fixed charge models of the solvent effects on this reaction may be highly inaccurate. These studies of the hydrogen peroxide reaction clearly indicate the directions which need to be taken by future studies in order to accurately characterize the SCW solvent effects on this reaction during SCWO processes.